

Crystallinity and Heats of Crystallization of Cellulose: A Microcalorimetric Investigation

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Synopsis

We have used a sensitive adiabatic microcalorimeter to study cellulose dissolution in its metal complex solvents cadoxen and ferric sodium tartrate (FeTNa). Heats of crystallization of cellulose I and II have thereby been estimated and range from -4.07 kcal/mol to -5.43 kcal/mol. A solvent-dependent heat of reaction factor has been invoked to explain differences in the heats of crystallization obtained by the two solvents. Conversion of cellulose I to cellulose II is an exothermic process with an enthalpy change of about -6.0 cal/g cellulose. The crystallinities of various cellulose samples have been determined using these thermodynamic data and have been found to be generally consistent with values given by more traditional means.

INTRODUCTION

Cellulose exists in several levels of molecular order or orientation in the fiber. A great variety of techniques (for example, X-ray diffraction, infrared spectroscopy, deuterium exchange, acid hydrolysis, iodine absorption, heats of wetting, sample density, and moisture regain) have shown that highly ordered crystalline regions in cellulose grade into amorphous areas. For a particular cellulose sample, the exact percentage of "crystalline" material as given by different techniques will seldom be in agreement.¹⁻⁵ In fact, the concept of only crystalline and noncrystalline regions in cellulose is itself an oversimplification, albeit a useful one. The different methods are consistent in that they place the samples in the same approximate order of crystallinity. Table I summarizes typical crystallinity values for a number of samples as given by various experimental techniques.

TABLE I
Crystallinity of Cellulosic Materials by Different Techniques

Technique	Typical crystallinities			
	Cotton	Wood pulp	Mercerized cotton	Viscose rayon
Deuteration	75-82	36-64	—	42
X-ray	70	—	65	39
Moisture regain	58	55	46	27
Iodine absorption	89-91	51-77	64-71	45
Infrared	62	—	58	42
Acid hydrolysis	86	81	71	45

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X-ray diffraction is generally considered the basic method for all such studies because of the direct relationship between the diffraction pattern and molecular order. However, it is possible to overestimate the crystalline fraction of cellulose by X-ray methods because of the predominant orientation or texture of these fibrous materials.⁴ Also X-ray techniques have been criticized as lacking sensitivity for more crystalline cellulosic materials such as cotton.¹ There are also conceptual problems with interpretation of X-ray data to obtain crystallinity values.⁵⁻⁹ Furthermore, even cellulose samples which have diffuse X-ray spectra, indicating completely amorphous material, may in fact have crystalline domains which are too small to give a diffraction peak.¹⁰ These points are raised only to show that additional methods for determining crystallinity in cellulose would not be frivolous. One potentially valuable approach to the problem of cellulose crystallinity, and indeed to the nature of cellulose itself, is via thermodynamics.

Let us examine two examples of cellulose of different crystallinity and dissolve them under identical conditions in the same solvent. The heat released by dissolving samples of A and B is given by

$$Q_A = -X_A(\Delta H_{CR}) + \Delta H_{AM} \quad (1)$$

$$Q_B = -X_B(\Delta H_{CR}) + \Delta H_{AM} \quad (2)$$

where

Q_A = heat of solution of sample A (cal/mol)

Q_B = heat of solution of sample B (cal/mol)

X_A = mole fraction crystalline material in sample A

X_B = mole fraction crystalline material in sample B

ΔH_{CR} = heat of crystallization of cellulose from the amorphous to the crystallized state (cal/mol)

ΔH_{AM} = heat of solution of completely amorphous cellulose in the solvent (cal/mol)

This approach was first described by Calvet and Hermans.¹¹

After experimental determination of Q_A and Q_B , we subtract eqs (1) and (2) to obtain

$$Q_A - Q_B = -(X_A - X_B)\Delta H_{CR} \quad (3)$$

If we have estimates of X_A and X_B from one of the techniques mentioned previously (X-ray, IR, etc.), we can determine ΔH_{CR} for cellulose. Also once we have established a value for ΔH_{CR} , we can determine the crystallinity of any other cellulose sample from eq. (3) by reference to the standard sample A.

EXPERIMENTAL

Experimental Equipment and Procedures

A Tronac, Inc. (Orem, Utah) Model 450 adiabatic calorimeter having a temperature sensitivity of $\pm 0.0001^\circ\text{C}$ was used in this work. Silvered and evacuated Dewar flasks having low heat leak characteristics are the quasiadiabatic reaction vessels.

The calorimeter consists of several parts. A water bath combined with a cooled heater and a PTC-40 temperature controller provide a constant-temperature environment for the completely immersed reaction vessel. The insert assembly, an immersible holder for the reaction vessel, is mounted in a hole in the water bath lid. Component parts of the insert assembly are the reaction vessel, the header plate to which the vessel is clamped and sealed from the water bath, a stirring motor and stirrer, thermistor, calibration heater, and the electrical junction box with two cables to connect to the electronics console. The calorimeter electronics console provides the thermistor Wheatstone bridge circuit, the calibration heater circuit, and controls.

A Data Precision Model 3500 digital multimeter is connected to the calorimeter to monitor important calorimeter variables. The multimeter can also monitor the reaction vessel temperature. Temperature changes within the reaction vessel are measured and displayed on a Hewlett-Packard Model 7100 B dual channel strip chart recorder.

The cellulose samples of interest (weighing approximately 20 mg) are placed in preweighed thin-wall ampoules and dried at 60°C and -100 kPa over Drierite (anhydrous CaSO₄). After drying, the samples are quickly transferred to a desiccator containing Drierite, allowed to cool, and then weighed and sealed. After sealing, the ampoules are placed in a special holder and immersed in the reaction vessel which has previously been filled with 40 mL of the desired cellulose solvent (either cadoxen or ferric sodium tartrate). The reaction vessel is then mounted on the insert assembly, and the entire apparatus lowered into the water bath.

The heat capacity of the reaction vessel and its contents is determined using the calibration heater according to instructions given by the manufacturer. After the initial heat capacity determination, the ampoule is crushed, and the contents are released. Reaction ensues, and the resulting temperature changes are measured. At the end of the experimental run, a final heat capacity of the vessel and contents is determined.

The cellulose solvent cadoxen was prepared by the method of Segal and Timpa¹² and stored under refrigeration in brown glass bottles. Another common cellulose solvent, ferric sodium tartrate (FeTNa), was prepared by the method of Valtassari,¹³ using ferric chloride instead of ferric nitrate nonahydrate as the iron source. The FeTNa also contained 5 g/L of excess sodium tartrate for stabilization. The FeTNa was stored at room temperature in polyethylene bottles. The cadoxen and FeTNa were prepared from reagent grade chemicals in a single batch which was used in all the experiments reported here.

The cellulosic materials used and their suppliers are given in Table II. These materials were used as received without further purification. The X-ray diffraction scans were graciously provided by Dr. Al French of the USDA Southern Regional Research Center. The crystallinity indices (CI) were computed as follows from the diffraction scans¹⁴:

$$CI = \frac{I_{200} - I_{AM}}{I_{200}} \times 100 \quad (\text{cellulose I}) \quad (4)$$

$$CI = \frac{I_{110} - I_{15.0^\circ}}{I_{110}} \times 100 \quad (\text{cellulose II}) \quad (5)$$

TABLE II
Cellulose Samples and Their Manufacturers

Material	Supplier
Avicel PH 101 (lot 1705)	FMC Corp.
Whatman CF 11	Whatman Corp.
Wood pulp type E-7	Buckeye Cellulose Corp.
Cotton linter pulp (Paper Grade 500)	Buckeye Cellulose Corp.
Bleached desized cotton cloth (TF #400)	Test Fabrics, Inc.
Viscose challis (TF #266)	Test Fabrics, Inc.
Mercerized cotton cloth (TF #400 M)	Test Fabrics, Inc.
High wet modulus rayon (ES 349C)	Avetex Fibers, Inc.
Tire yarn rayon	Courtaulds, Ltd.

RESULTS AND DISCUSSION

Effect of Drying on Heat Solution

All cellulosic materials contain some moisture which will affect their apparent heat of solution (via the heat of wetting). This parameter was studied by drying Avicel PH 101 for various periods of time at 60°C and -100 kPa pressure over Drierite in a vacuum oven. These dried samples were then dissolved in FeTNa. The results of this experiment are given in Figure 1. In less than 10 h, a plateau is reached beyond which further drying has no effect on the heat of solution of Avicel. A drying period of 72 h was established for all other samples. Spot checks at longer drying times showed the 72-h period to be adequate for other samples.

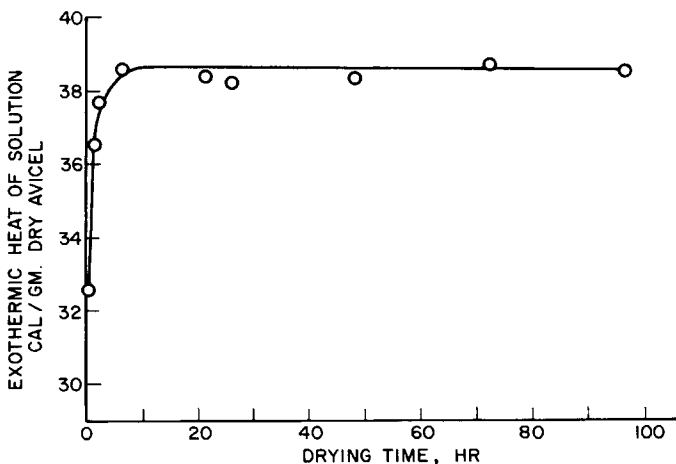


Fig. 1. Effect of drying time on heat of solution of avicel in FeTNa.

Effect of Ball Milling on the Heat of Solution

The amorphous cellulose standard was prepared by milling dry Avicel PH 101, lot 1705, in a Retsch rotary ball mill. The sealed grinding vessel was of agate and 50 10-mm diameter agate balls weighing about 70 g were used to grind 2.5 g of Avicel. A milling speed of approximately 400 RPM (80% of full speed) was used. The room temperature during grinding was around 22°C. Samples were taken from the grinding vessel at various times, placed in preweighed ampoules, dried for 72 h under the usual conditions and then cooled, weighed, and sealed. They were then dissolved in FeTNa. The results of this investigation are given in Figure 2. A constant heat of solution is obtained after about 50 h of grinding.

Heats of Crystallization of Cellulose I and II

The average heat of solution of dry crystalline Avicel is -38.5 cal/g and the corresponding value for thoroughly ball-milled Avicel is -57.3 cal/g. Avicel crystallinity prior to ball milling is about 75% by X-ray diffraction. After ball milling, there was no detectable X-ray crystallinity. Using these data, the heat of crystallization of cellulose I is -25.1 cal/g or -4.07 kcal/mol anhydroglucose units. As a check on this value, heat of solution runs were performed on crystalline and amorphous Avicel using cadoxen instead of FeTNa as the solvent. Heats of solution of crystalline and amorphous Avicel were -31.16 and -52.1 cal/g, respectively. A heat of crystallization of cellulose I of -27.4 cal/g was determined from eq. (3) with these data, about 9% higher than the value obtained using FeTNa as the solvent.

Heats of solution in cadoxen and FeTNa were also obtained for viscose challis, a sample of cellulose II which has an X-ray crystallinity of 44%. The X-ray diffraction patterns confirmed that the samples were essentially pure cellulose II. The average heats of solution in cadoxen and FeTNa were -37.6 and -43.6 cal/g, respectively. From these values, the heat of crystallization of cellulose II was calculated to be -31.3 cal/g (FeTNa) and -33.5 cal/g (cadoxen). The value for cadoxen is about 10% higher than the value for FeTNa, which is similar

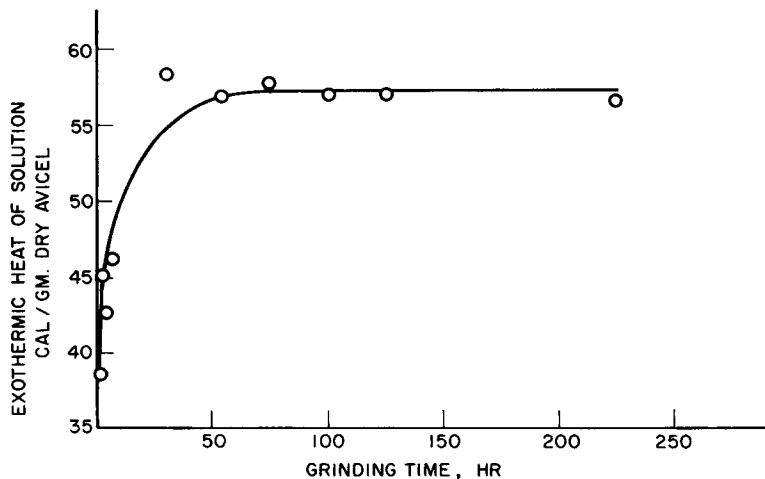


Fig. 2. Effect of ball milling time on heat of solution of avicel in FeTNa.

to the cellulose I result. These quantities were calculated using eq. (2) with heats of solution of amorphous cellulose, ΔH_{AM} , of -57.3 cal/g (FeTNa) and -52.1 cal/g (cadoxen) determined from the Avicel heat of solution data. The data given above are summarized in Table III. Possible explanations for the differences in heats of solution using the two solvents will be presented shortly.

Crystallinities of Cellulose Samples from Heats of Solution

The remaining samples listed in Table III were dried and their heats of solution in cadoxen were determined. The heats of crystallization of cellulose I and II in Table III were used with the resulting heat of solution data to estimate the percent crystallinity of these samples using eq. (2). There was no detectable cellulose II in the sample of mercerized cotton cloth, so the data for cellulose I were used to calculate the percent crystallinity of this sample. The average heats of solution, calculated percent crystallinity from eq. (2), and X-ray crystallinity values for each of these samples are given in Table IV.

The calorimetric and X-ray crystallinities are reasonably consistent, ranking the samples in the same approximate order. However, the range of crystallinities for this microcalorimetric technique is larger than the X-ray range, especially for the more highly crystalline cellulose I samples. Approximate agreement is probably all that can be expected, especially since X-ray crystallinity standards

TABLE III
Heats of Solution and Crystallization of Cellulose in Cadoxen and FeTNa

Heat of solution (cal/g of sample)	In cadoxen	In FeTNa
Dry crystalline Avicel	-31.6	-38.5
Dry amorphous Avicel	-52.1	-57.3
Dry viscose challis	-37.6	-43.6
Heat of crystallization [cal/g (kcal/mol)]		
Cellulose I	-27.4 (-4.44)	-25.1 (-4.07)
Cellulose II	-33.5 (-5.43)	-31.3 (-5.07)

TABLE IV
Heats of Solution and Crystallinities of Cellulose Samples

Sample	Heat of solution in cadoxen (cal/g)	Calculated crystallinity (%)	X-ray crystallinity (%)
Avicel (PH 101)	-31.6	standard	75
Wood pulp (Type E-7)	-36.4	57	72
Cotton cloth	-27.2	91	82
(bleached, desized TF # 400)			
Cotton linter pulp	-26.2	95	80
(Paper Grade 500)			
Mercerized cotton cloth	-28.1	88	80
(TF # 400M)			
Whatman CF11	-21.3	112	86
Viscose challis	-37.6	standard	44
(TF # 266)			
Tire cord rayon	-36.6	46	50
High wet modulus rayon	-35.2	50	52
(ES 349C)			

are required to establish the parameters for the microcalorimetric technique. The microcalorimetric technique appears to be more sensitive for the more crystalline samples than is the X-ray method. This may be an advantage of the microcalorimetric method. Recall that X-ray crystallinity methods have been criticized as lacking sensitivity for more crystalline materials such as cotton.

Estimate of Error in Heat of Crystallization Data

The reproducibility of the heat of solution values is approximately $\pm 2\%$. The X-ray crystallinity values are assumed to be accurate to within $\pm 1\%$. If these error estimates are accepted, then high and low values of the heat of crystallization of cellulose I and II in the two solvents are as given in Table V. These relatively large variations are a consequence of the fact that this technique requires subtracting two values which are reasonably close. This is, of course, a disadvantage of the calorimetric technique for crystallinity determination.

Hydrogen Bond Strength and Heat of Mercerization of Cellulose

Some interesting conclusions can be drawn from the data presented in Tables III and V. The average heat of crystallization of cellulose I is estimated at -4.44 kcal/mol anhydroglucose units (cadoxen). However, cellulose crystallization takes place by hydrogen bond formation between *two* anhydroglucose units so the total bond energy involved in cellulose crystallization is $2 \times -4.44 = -8.88$ kcal. If, as postulated, this bond energy is due to three hydrogen bonds (two intramolecular and one intermolecular), then the average hydrogen bond energy is about -3.0 kcal/mol.^{15,16} This is a fairly representative value for hydrogen bonds involving only oxygen and hydrogen.¹⁷⁻¹⁹ Using the approximate error data summarized in Table V, the hydrogen bond strength in cellulose I is between -2.5 and -3.3 kcal/mol. It is also of interest to note that the difference in heats of crystallization of cellulose I and II (equivalent to the heat of mercerization of cellulose) is in the range of -6.0 cal/g (see Table III) in cadoxen, or approximately -0.97 kcal/mol. Using other techniques, the heat of mercerization of cellulose has been variously estimated at between -2.0 cal/g and -9.1 cal/g.²⁰⁻²² The absolute order of cellulose decreases on mercerization (conversion of cellulose I to cellulose II) so that ΔS for the process is positive. A negative ΔH therefore implies a negative ΔG or spontaneous process.

TABLE V
Range of Heats of Crystallization of Cellulose I and II

Polymorph	Solvent	Heat of crystallization (cal/g)	
		Low	High
Cellulose I	FeTNa	23.0	28.0
Cellulose I	cadoxen	25.5	30.0
Cellulose II	FeTNa	27.2	35.8
Cellulose II	cadoxen	29.5	37.9

Potential Effects of Degree of Polymerization on Heats of Solution in Different Solvents

Experimental precision is on the order of $\pm 2\%$ for these ampoule runs, which may account for some of the discrepancy between the solvents. However, a more important source of error may arise in the differences in heats of chelation of cellulose samples of different degree of polymerization (DP).

The overall heat of solution of cellulose in these solvents can be viewed as composed of the following components:

- (1) heat of destruction of the crystalline lattice;
- (2) heat of wetting of amorphous cellulose;
- (3) heat of chelation of cellulose with solvent.

If the crystalline and amorphous cellulose standards were of the same DP, subtracting their heats of solution might be expected to eliminate this third component, which would be equal for both samples. However, ball milling Avicel will reduce its DP somewhat. In related investigations, we have found that the heats of reaction of both cadoxen and FeTNa are not the same for cellobiose and methyl β -D-glucose per glucose monomer unit.²³ Such differences may reasonably be assumed to exist for higher DP samples, e.g., Avicel which has a DP of about 200. This fact may account for the 8–10% divergence in the heats of crystallization obtained using different solvents. The heats of reaction of FeTNa with cellobiose and methyl β -D-glucose are higher than the corresponding values for cadoxen. This is exactly the pattern obtained for the crystalline and amorphous cellulose samples used here.

We are aware of only one other microcalorimetric study of cellulose dissolution in its metal complex solvents. The work cited gave heats of crystallization of cellulose I and II of -23.0 and -28.2 cal/g, respectively, and was done using completely wetted cellulose dissolved in cuprammonium.²² This points out again the apparent effect of the solvent on the heats of crystallization obtained. The value of -23.0 cal/g for the heat of crystallization of cellulose I corresponds to an average hydrogen bond strength in cellulose I of about -2.5 kcal/mol, comparable to our result. The heat of mercerization obtained²² was therefore

$$-28.2 - (-23.0) = -5.2 \text{ cal/g}$$

which is very close to the values obtained in our study.

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